

PATENT SPECIFICATION

NO DRAWINGS

L031839

L031839



Date of Application and filing Complete Specification Sept. 27, 1963.
No. 38236/63.

Application made in Germany (No. F38062 IVb/12o) on Oct. 17, 1962.

Complete Specification Published June 2, 1966.

© Crown Copyright 1966.

The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act, 1949 is Reinhard Schliebs, of 3, An der Joch, Koeln-Stammheim, Germany, of German nationality.

Index at acceptance: —C7 B(2C, 14, A1F)

—C 07 f 9/52

COMPLETE SPECIFICATION

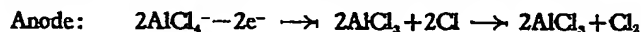
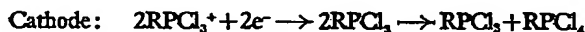
Process for the Electrolytic Production of Organic Phosphine Halides

We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT**, of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of organic phosphine halides by

electrolysis of complexes of organic phosphorus halides and aluminium halides.

It is known from the Journal of the Chemical Society, 1952, pages 3437—3445 that complexes of the general formula $[R\text{PCl}_2]^+ [Al_2Cl_7]^-$, in which R=alkyl, conduct electricity in solution in methylene chloride. If these complexes are decomposed electrolytically, the following cathode and anode reactions are to be expected:



With the passage of direct current, aluminium chloride is actually deposited on the anode. However, no products can be isolated at the cathode. In particular no chlorine is evolved.

If liquid complexes of the general formula $[R\text{PCl}_2]^+ [Al_2Cl_7]^-$ are used instead of a complex of the formula $[R\text{PCl}_2]^+ [AlCl_4]^-$ dissolved in methylene chloride, it is also possible to conduct large amounts of direct current through these complexes, also without the liberation of chlorine at the anode.

A process for the production of organic phosphine halides from organic phosphorus halide-aluminium halide complexes has now been found in which a phosphorus halide-aluminium halide complex of the formula $[RX\text{P}\text{Hal}_2]^+ [Al_2\text{Hal}_7]^-$, in which R represents a straight-chain or branched alkyl radical or a cycloalkyl radical, X=a chlorine or a bromine chain, or an alkyl radical, Hal=chlorine or bromine and the complex com-

prises only one halogen, n=1 or 2 and y=3n+1, is electrolysed in an electrolysis cell with cathode, anode and a diaphragm, in which said complex serves as catholyte, either as a melt or dissolved in a solvent, and an anhydrous melt of ion-conducting inorganic compounds is used as anolyte, the organic phosphine halide which is formed being isolated from the melt or solution. The electrolysis is carried out at temperatures above the melting point of the material in question. Depending on this material, temperatures of 60 to 250°C are used.

It is advantageous to use as anolytes melts of alkali metal-tetrahalogen-aluminates, although in principle it is also possible to employ other ion-conducting compounds, such as for example a melt of 2 mols. of sodium chloride and 1 mol. of ferric chloride or a solution of aluminium chloride in excess thionyl chloride. Among the complexes to be electrolysed, there are for example to be

[Price 4s. 6d.]

mentioned the following: ethyl tetrachlorophosphine-aluminium chloride complex, ethyl tetrachloro-phosphine-bis-aluminium chloride complex, diethyl trichlorophosphine-aluminium chloride complex and the corresponding bromine-containing complexes, e.g. $[\text{R}_3\text{PBr}_2]^+ [\text{Al}_2\text{Br}_7]^-$. Very suitable for this purpose are the complexes such as are produced according to French Patent Specification No. 1,372,192 by reacting a phosphorus halide with an alkyl or cycloalkyl chloride in a solution of aluminium chloride in alkali metal tetrachloroaluminates, at or above the melting temperature of these solutions.

The organophosphorus halide-aluminium chloride complex is in the cathode space, either in pure form or in a suitable solvent. Particularly suitable as solvents are the said alkali metal aluminium halides, but organic solvents such as methylene chloride or benzonitrile may also be used.

The nature of the electrolysis cell for carrying out the electrolysis is not critical. It is possible to use either V-shaped, U-shaped or H-shaped cells, in which the anode and cathode spacers are separated for example by a diaphragm consisting of fritted glass, glass fibre cloth or asbestos board. On the other hand, it is also possible to use trough-shaped cells in which clay crucibles serve as diaphragms. The diaphragms should be so dense that there is no substantial non-electrolytic exchange of material between the two spaces. The choice of the cathode material is of no great importance and iron, stainless steels or nickel are suitable for the purpose. When using alkali metal tetrachloroaluminate melts as anolyte, the choice of anode materials is, on the other hand, very limited. Whereas nickel or carbon in the form of charcoal or graphite can be used for a short time, only tungsten and silicon carbide can be employed for relatively long experiments.

The organic phosphine halides produced by the process can for example be used for the production of insecticides.

In order that the invention may be more fully understood, the following Examples are given, by way of illustration only:—

EXAMPLE 1

Into a stainless steel vessel equipped with a gas discharge pipe, a cooling jacket and a heating means, there was introduced a solution of 445 g. of $[\text{C}_2\text{H}_5\text{PCl}_2]^+ [\text{AlCl}_4]^-$ in 1555 g. of sodium tetrachloroaluminate, which solution was produced by reacting phosphorus trichloride and ethyl chloride in a melt of aluminium chloride and sodium tetrachloroaluminate, and a clay cell was suspended in this melt. The clay cell itself contained 965 g. of sodium tetrachloroaluminate. It was closed by a rubber plug having several drilled holes (gas discharge pipe, two tungsten anodes, thermometer). The clay cell and stainless

steel vessel were sealed off from one another by a rubber ring. The vessel was externally heated to 160°C ., the vessel was connected as the cathode and the tungsten electrode as the anode and the external heating again switched off. With a voltage of 7–9 volts, a current of 16 amps flowed and the temperature was kept by external cooling at 160 – 175°C . From the anode chamber, there was immediate vigorous evolution of chlorine. From the cathode chamber, ethyl dichlorophosphine distilled off after about 40 minutes. The experiment was stopped after the system had received 71.3 Amp. Hours. 67 g. of chlorine were formed and the current yield was 80.5%. During the experiment, 55 g. of ethyl dichlorophosphine were distilled off, and another 48 g. of ethyl dichlorophosphine were obtained by heating the cathode liquid *in vacuo* (12 mm.Hg.) to 200° , that is, a total of 103 g. This corresponds to a current yield of 59.3%. 260 g. of aluminium chloride were recovered from the anode space by heating *in vacuo*.

EXAMPLE 2

Instead of starting from the ethyl tetrachlorophosphine-aluminium chloride complex, it is also possible to employ the ethyl tetrachlorophosphine-bis-aluminium chloride complex.

In an electrolysis cell according to Example 1, a mixture of 551 g. of $[\text{C}_2\text{H}_5\text{PCl}_2]^+ [\text{Al}_2\text{Cl}_7]^-$ and 1072 g. of sodium tetrachloroaluminate was introduced into the cathode space and 990 g. of sodium tetrachloroaluminate into the anode space. Electrolysis was carried out under similar conditions to those of Example 1 and the experiment stopped after the system had received 58.5 Ah. During the experiment, no ethyl dichlorophosphine was distilled.

Chlorine yield: 77 g., theoretical

Aluminium chloride from the anode space: 218 g.

Ethyl dichlorophosphine by vacuum distillation of the cathode space:

a) without addition of common salt: 27.3 g.

b) with addition of common salt: 70.2 g = 97.5 g., 68.2% current yield.

EXAMPLE 3

For reasons of the electrical conductivity, it is desirable to dilute the complex that is to be reduced with alkali metal tetrachloroaluminate, but this is not absolutely necessary: a U-shaped cell, in which the cathode and anode spaces were separated by an inwardly flanged glass fibre diaphragm, contained a nickel tube as cathode and a bundle of 6 tungsten welding electrodes as anode. 267 g. of $[\text{C}_2\text{H}_5\text{PCl}_2]^+ [\text{Al}_2\text{Cl}_7]^-$ were placed in the cathode space and 265 g. of sodium-lithium tetrachloroaluminate (which starts to solidify at

about 110°) were placed in the anode space. Electrolysis was carried out at 150°C. and 0.5—0.6 amps until 840.80 Ah were absorbed. Yield: 21 g. of chlorine, 68% current yield and 22 g. of ethyl dichlorophosphine, 38.6% current yield.

EXAMPLE 4

The electrolytic reduction of the complex $[\text{CH}_3\text{PBr}_2]^+ [\text{Al}_2\text{Br}_7]^-$ was carried out in an electrolysis cell according to Example 3. 285 g. of the complex were introduced into the cathode space and 285 g. of sodium-lithium tetrachloraluminate into the anode space. Electrolysis was carried out at 155° and with 0.4—0.6 amps. There was no danger of the cathodically formed methyl dibromophosphine attacking the nickel cathode with formation of the complex $[\text{Ni}(\text{CH}_3\text{PBr}_2)_2]$, since this complex is not stable above 110°, (see L. Maier, Angew. Chem. 71, 574, 1959). The experiment was stopped after the system had received 12.9 Ah. The contents of the cathode space were distilled with addition of 35 g. of sodium bromide at 12 mm.Hg. and there were obtained 30 g. of methyl dibromophosphine, corresponding to a current yield of 60.6%. From the anode space, a mixture of 21.6 mol% of bromine with 78.4 mol % of chlorine were liberated during the electrolysis. Subsequent to the experiment, it was possible to obtain 61 g. of a mixture of 77.3 mol % of aluminium chloride and 22.7 mol % of aluminium bromide from the anode liquid *in vacuo*.

EXAMPLE 5

Using a V-shaped cell, in which the anode and cathode spaces were separated by a glass frit diaphragm and which had a nickel cathode and a tungsten anode, 195 g. of sodium tetrachloraluminate were introduced into the anode chamber and 195 g. of a mixture of $[(\text{C}_2\text{H}_5)_2\text{PCl}_2]^+ [\text{AlCl}_4]^-$ and sodium tetrachloraluminate (molar ratio 1:1) were introduced into the cathode space. The catholyte was prepared by reacting ethyl dichlorophosphine with ethyl chloride in a melt of aluminium chloride in sodium tetrachloraluminate and started to solidify from 67°. Electrolysis was carried out at 170° and with 1.3—1.9 amps until the system had received 32600 Amp. Secs=9 Amp. Hours. 11 g. of chlorine were developed and the current yield was 92%. The contents of the cathode space were distilled with 50 g. of potassium chloride and a distillate was obtained which contained 5.4 g. of diethyl chlorophosphine, Bp_{1.10 mm.} 82°C. This corresponds to a current yield of 25.4%. No analysis of the anolyte was made.

EXAMPLE 6

Using an H-shaped cell, in which both vertical tubes can be heated independently of one another, and which has a nickel cathode

and a tungsten anode, 330 g. of sodium-lithium tetrachloraluminate were introduced into the anode space and 250 g. of a mixture of 2 mols of sodium tetrachloraluminate with 1 mol of cyclohexyl tetrachlorophosphine-aluminium chloride complex were introduced into the cathode space. The catholyte had been prepared by reacting phosphorus trichloride and cyclohexyl chloride with a solution of aluminium chloride in sodium tetrachloraluminate. A G 3 frit was situated in the horizontal part of the cell. The anode space was heated to 160—170° and the cathode space to 60—64°. Electrolysis was carried out with about 0.135 amp until the system had received about 9 Ah. The content of the cathode space was thereafter distilled with 60 g. of potassium chloride, 12 g. of crude cyclohexyl dichlorophosphine being obtained.

By distillation, 9 g of the pure compound were recovered (Bp_{3 mm.} 55°. chlorine=38.6%). This corresponds to a current yield of 29%.

The low yields in some of the Examples are to be attributed to the fact that in this case small cells were used, in which stirring could not be carried out. As a result, there was over-reduction at the cathode (deposition of organically substituted metal phosphides etc.) which naturally reduce the yield.

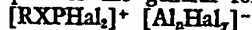
EXAMPLE 7

1570 g. of a melt consisting of equal parts of the complexes $[\text{CH}_3\text{PCl}_2]^+ [\text{AlCl}_4]^-$ and $[\text{CH}_2\text{PCl}_2]^+ [\text{Al}_2\text{Cl}_7]^-$ were electrolysed with vigorous stirring in a glass cell, which was fitted with stirrers for the cathode and the anode space.

387 g. of methyldichlorophosphine was obtained for 205 Ah which went into the system and 265 g. of chlorine was evolved, corresponding to a current yield of 86.5%.

WHAT WE CLAIM IS:—

1. A process for producing organic phosphine halides which comprises electrolysing, as a catholyte in an electrolysis cell having a diaphragm, a phosphorus halide-aluminium halide complex of the general formula



in which R is an alkyl radical or a cycloalkyl radical, X is a chlorine or bromine atom or an alkyl radical, Hal is chlorine or bromine and the complex comprises only one halogen, n is 1 or 2 and y is 3n+1, and electrolysing as an anolyte an anhydrous melt of an ion-conducting inorganic compound, the electrolysis being effected in the molten state at a temperature of 60 to 250°C and recovering the organic phosphine halide formed.

2. A process as claimed in claim 1 in which the ion-conducting inorganic compound is an alkali metal tetrahalogen aluminate.

3. A process as claimed in claim 1 in which

the ion-conducting inorganic compound is a mixture of sodium chloride and ferric chloride.

4. A process as claimed in any of claims 1 to 3 in which the electrolysis is carried out in a catholyte containing a solvent for the organophosphorous halide-aluminium halide complex.

5. A process as claimed in claim 4 in which the solvent is an alkali metal aluminium halide.

6. A process as claimed in claim 4 in which the solvent is methylene chloride.

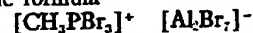
7. A process as claimed in claim 4 in which the solvent is benzonitrile.

8. A process as claimed in claim 5 for the production of ethyl dichlorophosphine which comprises electrolysis as a catholyte in an electrolysis cell having a diaphragm a complex of the formula

9. A process as claimed in claim 4 in which the solvent is an alkali metal aluminium halide and electrolysis as an anolyte a melt of sodium-lithium tetrachloro-aluminate at a temperature of 160 to 175°C and recovering the methyl-dibromophosphine formed.

of 160 to 175°C and recovering the ethyl dichlorophosphine formed.

9. A process as claimed in claim 1 for the production of methyl-dibromophosphine which comprises electrolysis as a catholyte in an electrolysis cell having a diaphragm a complex of the formula



and electrolysis as an anolyte a melt of sodium-lithium tetrachloro-aluminate at a temperature of 160 to 175°C and recovering the methyl-dibromophosphine formed.

10. A process for the production of organic phosphine halides substantially as herein described with reference to the Examples.

11. Organic phosphine halides when produced by a process as claimed in any of claims 1 to 10.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52-54, High Holborn,
London, W.C.1.